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B.A. Trofimov on the 65th Anniversary of His Birth

3,3-Dimethyl-2,3,5,6-tetrahydroimidazo[2,1-*b*][1,3,4]thiazasilole and Its Derivatives with Five-Coordinate Silicon Atom

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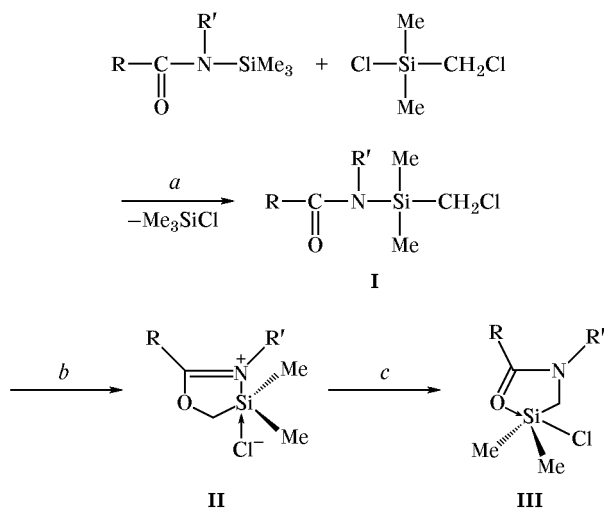
Abstract—Previously unknown 3,3-dimethyl-2,3,5,6-tetrahydroimidazo[2,1-*b*][1,3,4]thiazasilole and its zwitterionic derivatives containing five-coordinate silicon atom, namely 7-substituted 3,3-dimethyl-2,3,5,6-tetrahydroimidazo[2,1-*b*][1,3,4]thiazasilol-4-ium chlorides, have been synthesized by reaction of 1,3-bis-(trimethylsilyl)tetrahydroimidazole-2-thione with chloro(chloromethyl)dimethylsilane and subsequent transformations of the products.

Reactions of *N*-trimethylsilyl derivatives of amides, lactams, and ureas with chloro(chloromethyl)dimethylsilane were recommended as a convenient method for preparation of the corresponding O→Si-chelated *N*-chloro(dimethyl)silylmethyl derivatives of five-coordinated silicon [1, 2]. Their formation involves three consecutive steps: (a) spontaneous transsilylation of the initial reactants; (b) kinetically controlled

intramolecular *O*-silylmethylation of *N*-chloromethyl-(dimethyl)silyl intermediate **I**; and (c) thermodynamically controlled specific Chapman rearrangement of zwitterionic “isoamide” derivative **II** into final “amide” **III** (Scheme 1).

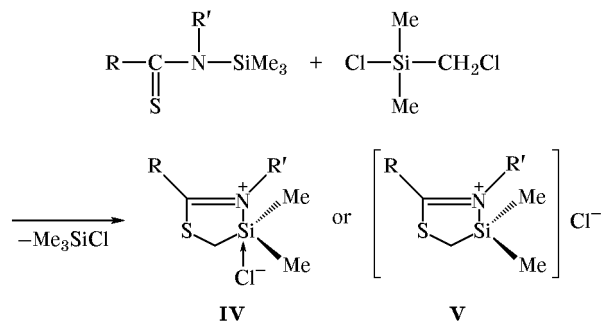
Analogous reactions of *N*-trimethylsilyl thioamides were studied only with *N*-trimethylsilyl derivatives of 2-pyrrolidinethione [3, 4] and *N,N*-diethyl-*N'*-methylthiourea [5]. Unlike the amide derivatives, in these cases the process is terminated at the stage of S-silylmethylation which gives zwitterionic derivatives of *S*-chloromethyl(dimethyl)silyl isothiolactams **IV** and ionic isothiuronium salt **V** (Scheme 2).

Scheme 1.



R, R' = Alk; RR' = (CH₂)_n, n = 3–5; R = NAlk, R' = H, Alk.

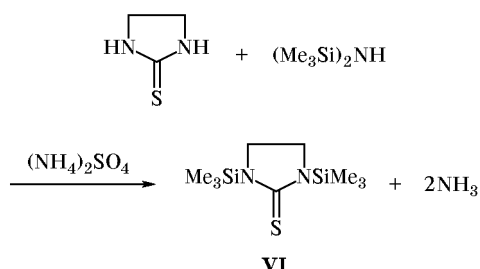
Scheme 2.



IV, RR' = (CH₂)₃; **V**, R = NEt₂, R' = Me.

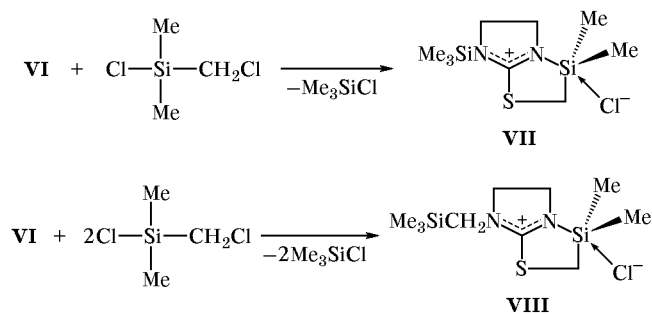
The pronounced biological activity [6, 7] and stability of the “isothioamide” derivatives to rearrangement into “thioamide” structures have stimulated our further research in this line. We examined the structure and reactivity of previously unknown products of the reaction of chloro(chloromethyl)dimethylsilane with 1,3-bis(trimethylsilyl)-2-imidazolidinethione (**VI**) (for preliminary communications, see [8–10]). Initial compound **VI** was prepared by reaction of 2-imidazolidinethione with excess hexamethyldisilazane in the presence of a catalytic amount of ammonium sulfate (Scheme 3). Unlike the synthesis of **VI** via stepwise reaction of 2-imidazolidinethione with 2 equiv of chlorotrimethylsilane in the presence of triethylamine [11], the above procedure ensured almost quantitative yield of the target product.

Scheme 3.



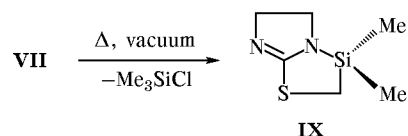
Heating of an equimolar mixture of compound **VI** with chloro(chloromethyl)dimethylsilane over a period of 30 min and removal of the released chlorotrimethylsilane by distillation gave bicyclic zwitterionic 3,3-dimethyl-7-trimethylsilyl-2,3,5,6-tetrahydroimidazo[2,1-*b*][1,3,4]thiazasilol-4-ium chloride (**VII**) (Scheme 4). Structurally related 7-chloro(dimethyl)silylmethyl derivative **VIII** was obtained by prolonged (6 h) heating of compound **VI** with 3 equiv of chloro(chloromethyl)dimethylsilane, other conditions being equal (Scheme 4). Compounds **VII** and **VIII** are colorless crystalline substances which are extremely sensitive to atmospheric moisture. Chloride **VII** is

Scheme 4.



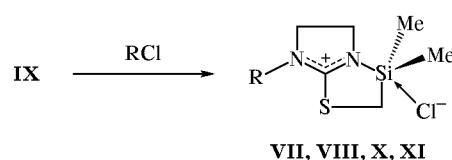
thermally unstable. On heating under reduced pressure it loses chlorotrimethylsilane molecule, yielding 3,3-dimethyl-2,3,5,6-tetrahydroimidazo[2,1-*b*][1,3,4]-thiazasilole (**IX**) (Scheme 5).

Scheme 5.



A fairly high basicity of the N³ nitrogen atom in molecule **IX** facilitates its reactions with electrophiles. Addition of a saturated solution of hydrogen chloride in diethyl ether to compound **IX** leads to formation of hydrochloride **X**. After removal of volatile components, compound **X** was isolated as a low-melting finely crystalline powder which quickly softens on exposure to air. According to the NMR data, prolonged heating of a mixture of compound **IX** with excess chlorotrimethylsilane or chloro(chloromethyl)dimethylsilane gives compounds **VII** and **VIII**, respectively. Likewise, by reaction with benzyl chloride compound **IX** was converted into zwitterionic 7-benzyl-3,3-dimethyl-2,3,5,6-tetrahydroimidazo[2,1-*b*][1,3,4]thiazasilol-4-ium chloride (**XI**) which was detected by NMR spectroscopy (Scheme 6). We failed to isolate product **XI** from the reaction mixture because of its hydrolytic instability.

Scheme 6.



VII, R = Me₃Si; **VIII**, R = Me₃SiCH₂; **X**, R = H;
XI, R = PhCH₂.

The structure of the products was proved by the ¹H, ¹³C, and ²⁹Si NMR spectra (see table), as well as by the IR and mass spectra. Compounds **VII**, **VIII**, **X**, and **XI** should be regarded as 7-substituted 3,3-dimethyl-2,3,5,6-tetrahydroimidazo[2,1-*b*][1,3,4]thiazasilol-4-ium inner salts. The presence of a five-coordinate silicon atom in their molecules unambiguously follows from considerable upfield shifts of the ²⁹Si signals relative to that observed for completely ionized isothiuronium salt **V** (δ_{Si} 36 ppm) [5]. On heating of solutions of **VII** and **VIII**, the magnitude of the upfield shift increases, indicating increase in the five-coordinate character of the silicon atom. Such

¹H, ¹³C, and ²⁹Si NMR spectra (δ, ppm) of compounds **VI–XI**

| Comp. no. | Nucleus | MeSi (N) | MeSi (S) | SiCH ₂ S | SiCH ₂ N | 5-CH ₂ | 6-CH ₂ | C=N (C=S) |
|-------------|------------------------------|----------|--------------------------|---------------------|---------------------|-------------------|-------------------|-----------|
| VI | ¹ H | 0.40 s | | | | 3.59 s | 3.59 s | 191.32 |
| | ¹³ C | 0.29 | | | | 48.41 | 48.41 | |
| | ²⁹ Si | 8.57 | | | | | | |
| VII | ¹ H | 0.46 s | 0.68 s | 2.97 s | | 3.96 m | 4.34 m | 179.26 |
| | ¹³ C | -1.39 | -1.13 | 17.72 | | 44.65 | 52.91 | |
| | ²⁹ Si | 8.2 | 17.6 (12.8) ^a | | | | | |
| VIII | ¹ H | 0.65 s | 0.70 s | 3.04 s | 3.35 s | 4.05 m | 4.44 m | 177.98 |
| | ¹³ C | 0.82 | -1.08 | 18.07 | 41.51 | 44.93 | 56.98 | |
| | ²⁹ Si | 26.5 | 20.3 (16.5) ^a | | | | | |
| IX | ¹ H | | 0.37 s | 2.43 s | | 3.44 m | 4.18 m | 171.0 |
| | ¹³ C | | -1.71 | 16.1 | | 43.94 | 61.3 | |
| | ²⁹ Si | | 14.0 | | | | | |
| X | ¹ H | | 0.64 s | 2.83 s | | 3.92 m | 4.21 m | |
| | ²⁹ Si | | 15.2 (10.1) ^a | | | | | |
| XI | ¹ H ^b | | 0.71 | 3.04 | | 3.81 m | 4.20 m | 171.9 |
| | ¹³ C ^c | | -0.61 | 19.05 | | 45.0 | 53.73 | |
| | ²⁹ Si | | 10.1 (4.8) ^a | | | | | |

^a At 60°C.^b Other signals, δ, ppm: 4.58 s (CH₂Ph), 7.32 m (Ph).^c Other signals, δ_C, ppm: 51.6 (CH₂Ph), 128.4 (C^p), 129.0 (C^o), 129.2 (C^m), 132.8 (Cⁱ).

a behavior is typical of only zwitterionic derivatives of a trigonal–bipyramidal silicon atom [1, 2]. Therefore, we can conclude with certainty that the silicon atom in molecules **VII**, **VIII**, **X**, and **XI** is linked to the N⁴ atom through a covalent bond, and with chloride ion, through a dative bond. The existence of that bond in structures **IV**, **VII**, **VIII**, **X**, and **XI** and its absence in salt **V** may be interpreted in terms of the lower basicity of the *sp*²-hybridized nitrogen atom in hypothetical *S*-chloro(dimethyl)silylmethyl isothioamide resonance forms of the above zwitterionic compounds, as compared with the corresponding resonance structure of salt **V**. Therefore, the Si–N bond in **IV**, **VII**, **VIII**, **X**, and **XI** is weaker than in **V**, and the lower order of that bond provides the possibility for additional binding with chloride ion.

EXPERIMENTAL

The NMR spectra of compounds **VI–XI** were recorded from 5–10% solutions in CDCl₃ using JEOL FX-90Q and Bruker DPX-400 spectrometers; tetramethylsilane was added as internal reference. The IR spectra were recorded from KBr pellets or thin films on a Specord 75IR instrument. The mass spectra were run on an LKB-2091 mass spectrometer with direct sample admission into the ion source (electron impact,

10 and 60 eV; ion source temperature 250°C; inlet probe temperature 100–350°C).

1,3-Bis(trimethylsilyl)-2-imidazolidinethione (VI). A mixture of 5.1 g (0.05 mol) of 2-imidazolidinethione, 22 ml (0.14 mol) of hexamethyldisilazane, and a catalytic amount of ammonium sulfate was heated for 5 h under reflux (until ammonia no longer evolved). The mixture was cooled, and the precipitate was filtered off, washed with anhydrous diethyl ether, and dried under reduced pressure. Yield 12.1 g, mp 137–138°C [11]. IR spectrum, ν, cm⁻¹: 1350 (C=S); 1250, 840, 750 (SiMe₃, Si–N).

3,3-Dimethyl-7-trimethylsilyl-2,3,5,6-tetrahydroimidazo[2,1-*b*][1,3,4]thiazasilol-4-ium chloride (VII). A mixture of 1.1 g (0.04 mol) of compound **VI** and 0.6 g (0.04 mol) of chloro(chloromethyl)dimethylsilane was heated for 30 min at the boiling point. The released chlorotrimethylsilane was removed under reduced pressure to leave 1.1 g (100%) of compound **VII**, mp 85–87°C (decomp.). Mass spectrum, *m/z* (*I*_{rel.}, %): 172 (100) [*M* – Me₃SiCl]⁺, 115 (10) [C₄H₇N₂S]⁺, 102 (68) [C₃H₆N₂S]⁺, 93 (20) [Me₂SiCl]⁺, 84 (29) [C₄H₈N₂]⁺, 73 (25) [Me₃Si]⁺, 36 (32) [HCl]⁺. IR spectrum, ν, cm⁻¹: 1540 (C=N); 480 (Si–Cl); 750, 800–840, 1250 (SiMe₃, SiMe₂, Si–N). Found, %: C 38.60; H 7.65; N 10.49; S 11.22.

$C_9H_{21}ClN_2SSi_2$. Calculated, %: C 38.61; H 7.56; N 10.0; S 11.45.

7-Chloro(dimethyl)silylmethyl-3,3-dimethyl-2,3,5,6-tetrahydroimidazo[2,1-*b*][1,3,4]thiazasilol-4-ium chloride (VIII). A mixture of 4.4 g (0.02 mol) of compound VI and 10 ml (0.07 mol) of chloro-(chloromethyl)dimethylsilane was heated for 6 h at the boiling point. Volatile components were removed, and the solid residue was washed with heptane and dried under reduced pressure. Yield almost quantitative, mp 53–55°C. Mass spectrum, m/z (I_{rel} , %): 314 (5) M^+ , 208 (14) $[M - 106]^+$, 193 (13), 181 (11), 172 (17), 93 (100). IR spectrum, ν , cm^{-1} : 1570 (C=N), 480 (Si–Cl), 800–820 (SiMe₂), 840 (Si–N). Found, %: C 34.52; H 6.44; N 8.72; S 9.87; Si 17.47. $C_9H_{20}Cl_2N_2SSi_2$. Calculated, %: C 34.27; H 6.39; N 8.88; S 10.17; Si 17.81.

3,3-Dimethyl-2,3,5,6-tetrahydroimidazo[2,1-*b*][1,3,4]thiazasilole (IX). Compound VII, 4.5 g (0.02 mol), was heated for 1 h at 80–90°C under reduced pressure (4 mm) to remove chlorotrimethylsilane. The residue was compound IX. Yield 2.5 g (67%), viscous liquid, bp 129–130°C (1.5 mm). Mass spectrum, m/z (I_{rel} , %): 172 M^+ . IR spectrum, ν , cm^{-1} : 1550 (C=N), 800–820 (SiMe₂), 840 (Si–N). Found, %: C 42.15; H 7.43; N 15.87; S 18.64; Si 16.02. $C_6H_{12}N_2SSi$. Calculated, %: C 41.82; H 7.02; N 16.25; S 18.60; Si 16.30.

3,3-Dimethyl-3,5,6,7-tetrahydro-2H-imidazo[2,1-*b*][1,3,4]thiazasilol-4-ium chloride (X). A saturated solution of hydrogen chloride in 10 ml of diethyl ether was added to 2.4 g of compound IX. The precipitate was filtered off and dried under reduced pressure. mp 63–65°C. IR spectrum, ν , cm^{-1} : 1550 (C=N), 480 (Si–Cl). Mass spectrum, m/z (I_{rel} , %): 172 (100) $[M - HCl]^+$, 36 (20) $[HCl]^+$. Found, %: Cl 16.62; N 13.77; S 15.31. $C_6H_{13}ClN_2SSi$. Calculated, %: Cl 16.98; N 13.41; S 15.36.

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